MTBE-ONLY GROUNDWATER RELEASES

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SAM Forum & Symposium on MTBE and other Oxygenates

September 25, 2002
San Diego, CA

CONTAINS

MTBE

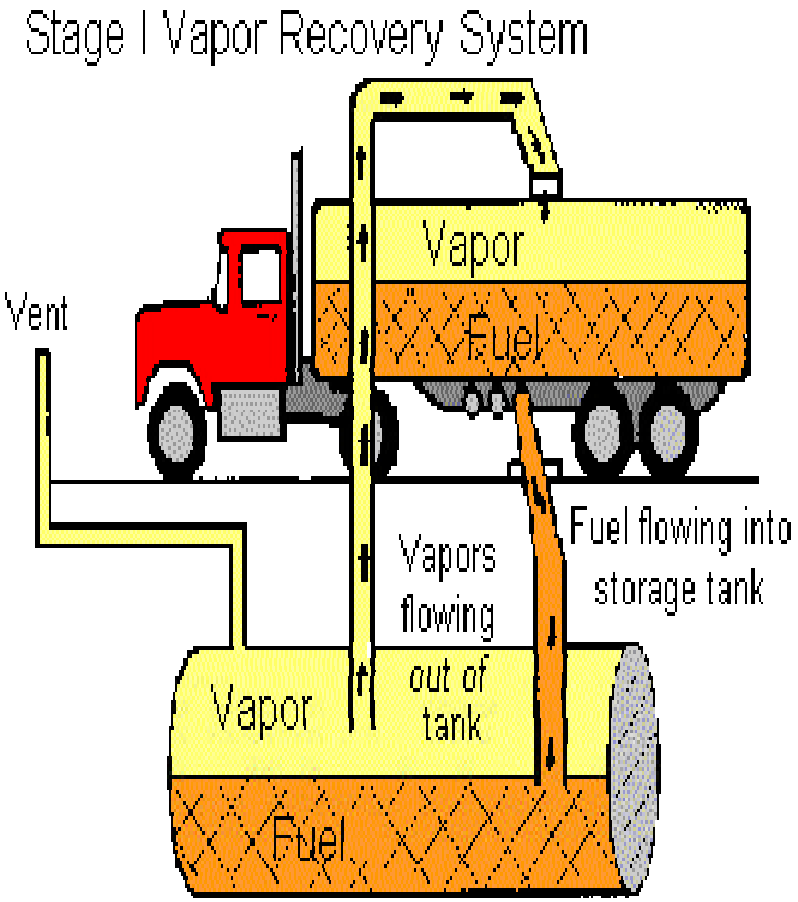
THE STATE OF CALIFORNIA HAS DETERMINED
THAT THE USE OF THIS CHEMICAL PRESENTS
A SIGNIFICANT RISK TO THE ENVIRONMENT

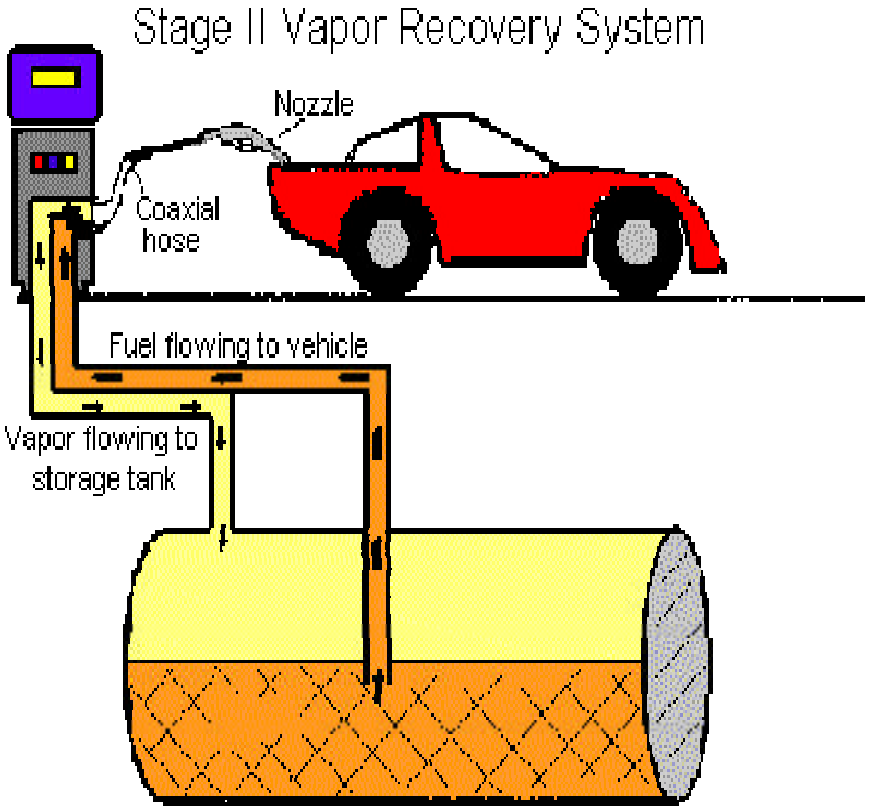
UST Release Scenarios

- **Catastrophic Release of Gasoline**
- **Gasoline Release**

  w/ retained PSH (“soils-only” release)
- **Vapor**
- **All of the above**

UST Vapor Systems





Vapor Problems?

Underground Storage Tank System Field-Based Research Project Report, submitted to SWRCB May 31, 2002

- 182 UST upgraded Systems tested
- 61% had detectable vapor leaks
- Majority of leaks in tank excavation
- Many detected at tank top (fill/vent risers)
- None likely exceeded UST integrity test standard of 0.1 gph (2.4 gallons/day….)
- Hear more from SWRCB at 1:40 today!

The Great Escape, 1

LUSTLine Bulletin 30, by Blayne Hartman (www.tegenv.com)

What vapors are coming out of the UST?

First…Calculate vapor pressures of gasoline compounds

$$P_i = VP_i * MF_i$$

Vp_i, is the Vapor Pressure of component i

MF_i, is the Mole Fraction of component i

The Great Escape, 2

Then...Convert Pressures into relative concentrations

$$C_i = VP_i * MW_i * MF_i / RT$$

C_i, concentration (mass/liter) of component i

MW_i, molecular weight of component i

MF_i, is the mole fraction of component i

RT, is the universal gas constant times temperature

The Great Escape…of MTBE

	VP (atm)	MW (g/M)	MF	C_{vapor} (ug/L)
Benzene	0.13	78	0.025	10,600
MTBE	0.32	88	0.125	147,000
Alkanes (C4-C8)	0.2	100	0.50	400,000

Chronic Release "soils-only" w/ PSH

- Residual gasoline in vadose zone
- Soils are now the "UST"
- Calculation is the same as for the UST
- Apply Equation 6-13 in SAM Manual and in vapor risk spreadsheet

  (for TPH >100 mg/kg)

MTBE Vapor and Water

Ref: SAM Manual

Multiphase Equilibrium

$C_{total} = C_{vapor} + C_{water} + C_{soil}$ (…+C_{PSH})

…..+ PSH as condensate…?

$C_{vapor} = H\ C_{water}$ $C_{soil}=K_{oc}\ F_{oc}\ C_w$

	H, (d'less)	S, mg/L	K_{oc}
Benzene	0.23	1800	62
MTBE	0.024	48,000	78

“Example Soil”

Strategies for Characterizing subsurface Releases of Gasoline containing MTBE, API, August 2000, No. 11

- Calculated equilibrium distribution of Benzene and MTBE in an unsaturated soil
- Note: persistence of MTBE vapor

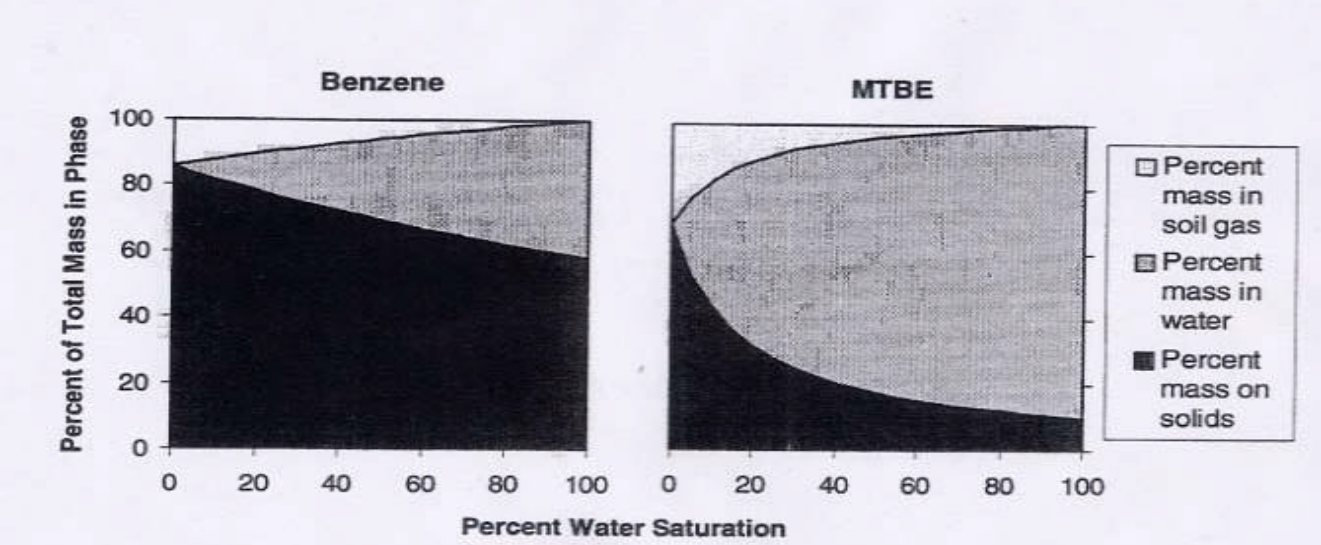


Figure 1: Equilibrium Partitioning of Benzene and MTBE in an Example Soil

Vapor Movement, 1

Blayne Hartman, LUSTLine Bulletin 28/ SAM Manual

- In absence of recharge, vapors will diffuse
- Effective Diffusivity

$$D_e = D_{air} (\Theta_{air}^{10/3} / \Theta_{total}^{2}) \qquad \text{(SAM Manual)}$$

For MTBE, SAM default soil

$\Theta_{air} = 0.20$

$\Theta_{total} = 0.30$

$D_{air} = 0.08$

$D_e = 0.00418\ cm^2/sec$

Vapor Movement, 2

Blayne Hartman, LUSTLine Bulletin 28

- Diffusive velocity: no advection or recharge
- Distance over time (w/continuous source strength)

$$\text{Distance} = (2 * D_e * \text{time})^{1/2}$$

D_e = 0.00418 cm^2/sec for MTBE; time = 1 year

Distance = 513 cm (17 feet) per year

……Direct Implications for shallow groundwater MTBE-only release from vapor phase

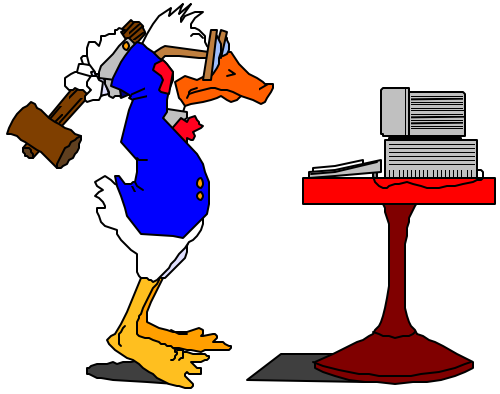
Vadose Zone Transport

Simulation of Transport of MTBE to Groundwater From Small-Volume Releases of Gasoline in the Vadose Zone.
Lahvis and Rehmann API Research Bulletin, June 2000, no. 10

- Based on USGS Model R-UNSAT
  by Matthew Lahvis and Arthur Baehr
- Multi-species transport
- Variable moisture content
- Diffusion, recharge, sorption
- O_2 and biodegradation

Thanks to Dr. Matt Lahvis, Shell Global Solutions (US) Inc. for following graphics

WHAT DO WE KNOW APRIORI
(MTBE vs. C_6H_6)



- source composition
- phase-partitioning properties
- principal transport mechanisms

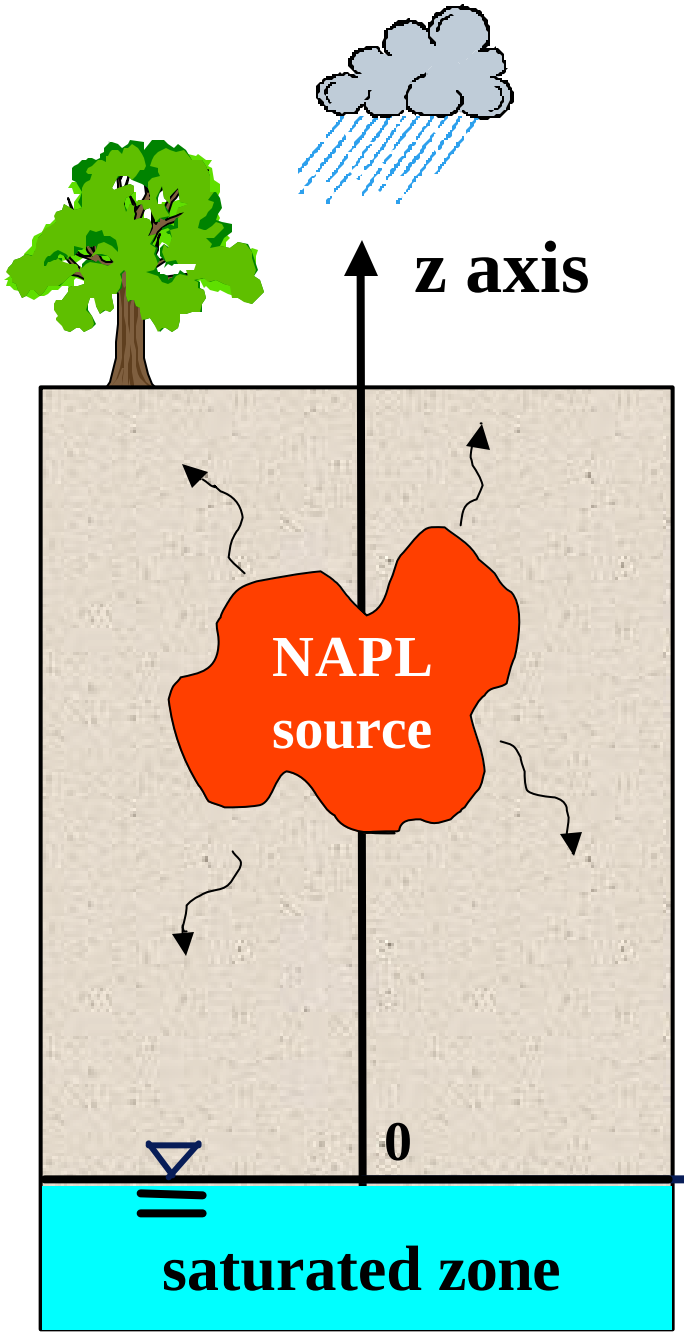
Lahvis and Rehmann, 2000

ASSUMPTIONS

- source is immobile
- MTBE is non reactive, benzene is reactive
- hydrostatic moisture distribution
- soil properties (van Genuchten)
- equilibrium partitioning

Lahvis and Rehmann, 2000

BOUNDARY CONDITIONS



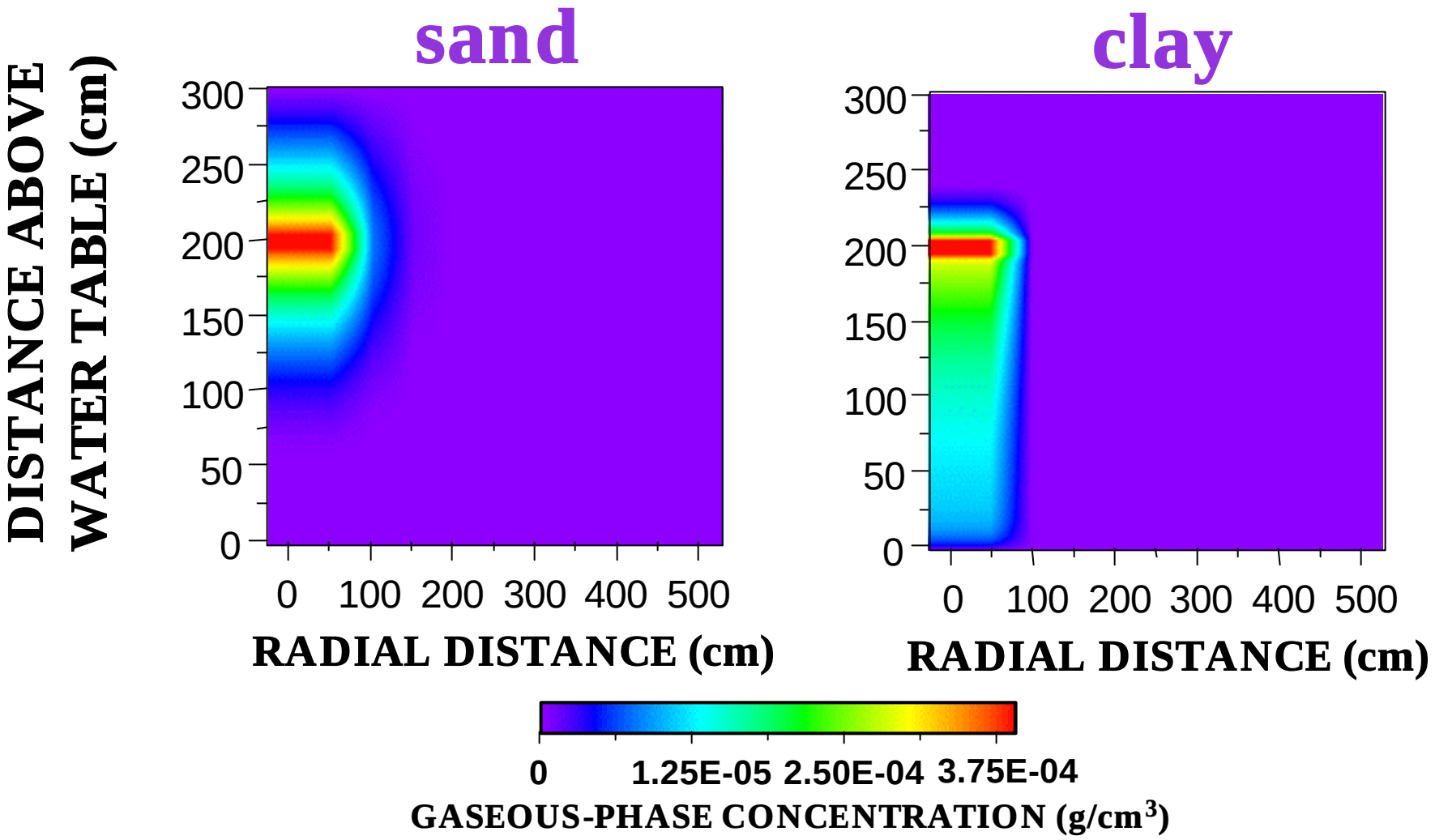
LAND SURFACE - atmospheric

SOURCE - constant concentration
- time dependent

WATER TABLE - MTBE, C_6H_6 : C = 0
O_2: impermeable

Lahvis and Rehmann, 2000

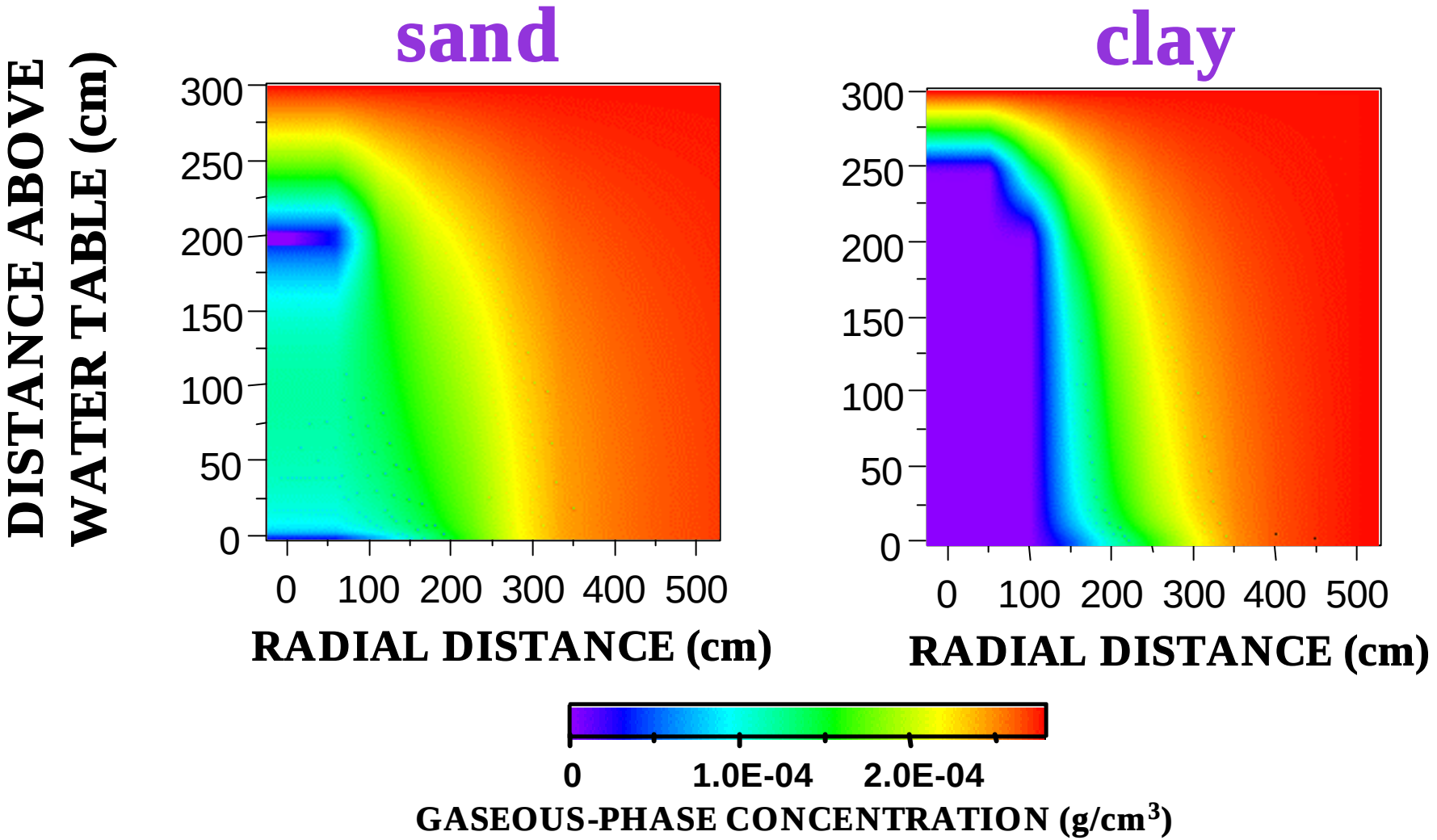
C_6H_6 DISTRIBUTION: CHRONIC RELEASE
(infiltration rate = 20 cm/yr)



Lahvis and Rehmann, 2000

O_2 DISTRIBUTION: CHRONIC RELEASE

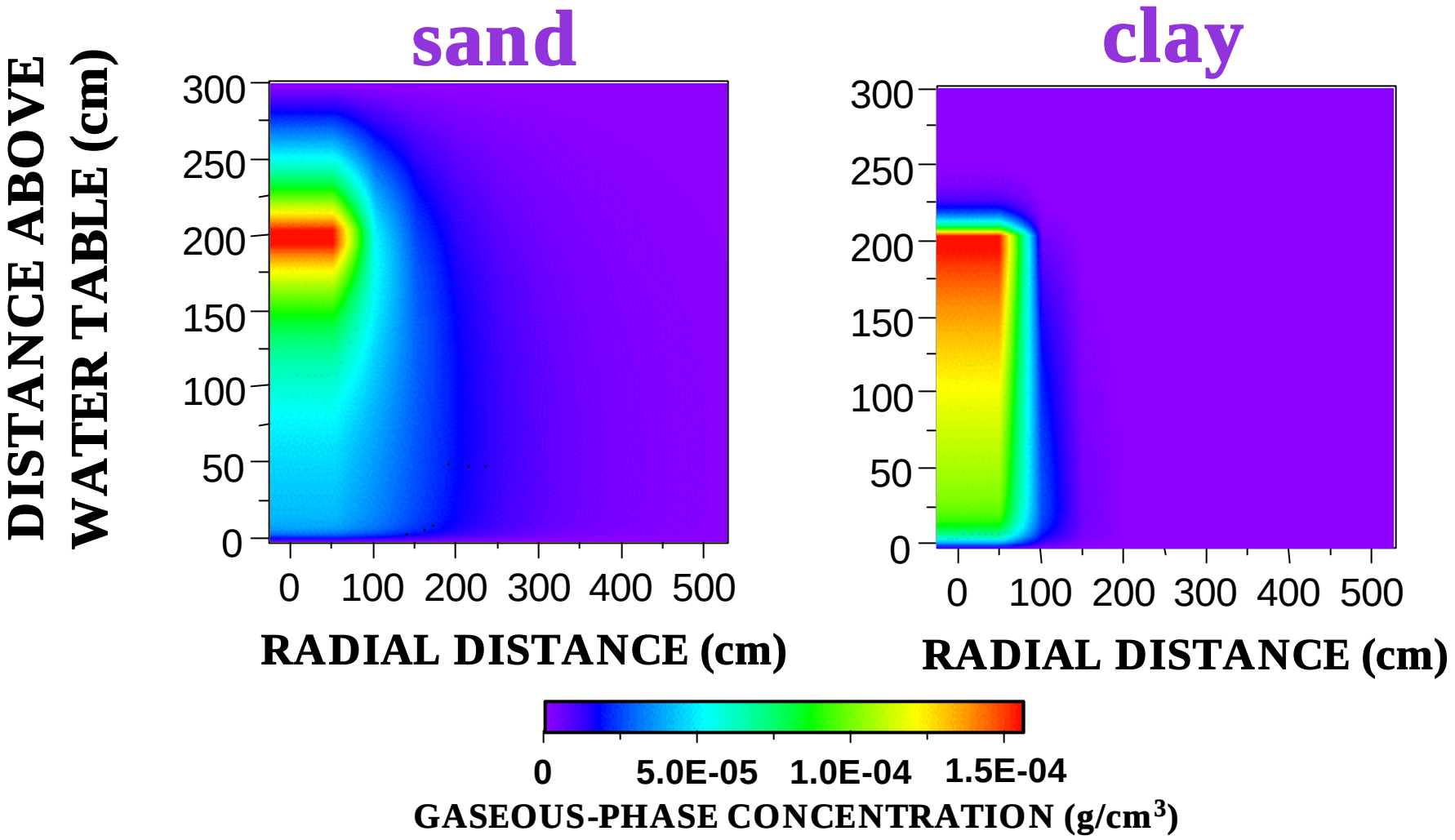
(infiltration rate = 20 cm/yr)



Lahvis and Rehmann, 2000

MTBE DISTRIBUTION: CHRONIC RELEASE

(infiltration rate = 20 cm/yr)



Lahvis and Rehmann, 2000

WHAT WE LEARNED

- **enrichment in MTBE relative to benzene**
  -- potential for ppm concentrations (chronic)
- **capillary zone limits mass transport**
- **diffusion to the atmosphere - significant mass-loss pathway**
- **breakthrough times variable**

Lahvis and Rehmann, 2000

Highlights: Gasoline Release w/ MTBE

- MTBE preferentially released as vapor from UST
- MTBE:Benzene > 10 in vapor
- “soils-only” case also leads to preferential release of MTBE vapor
- MTBE Vapor Can Move Quickly, > 10 ft/yr
- Vadose zone recharge and biodegradation ‘enrich’ water phase relative to MTBE
- If BTEX and MTBE in groundwater, expect PSH (also consider if no O_2)

Local Examples

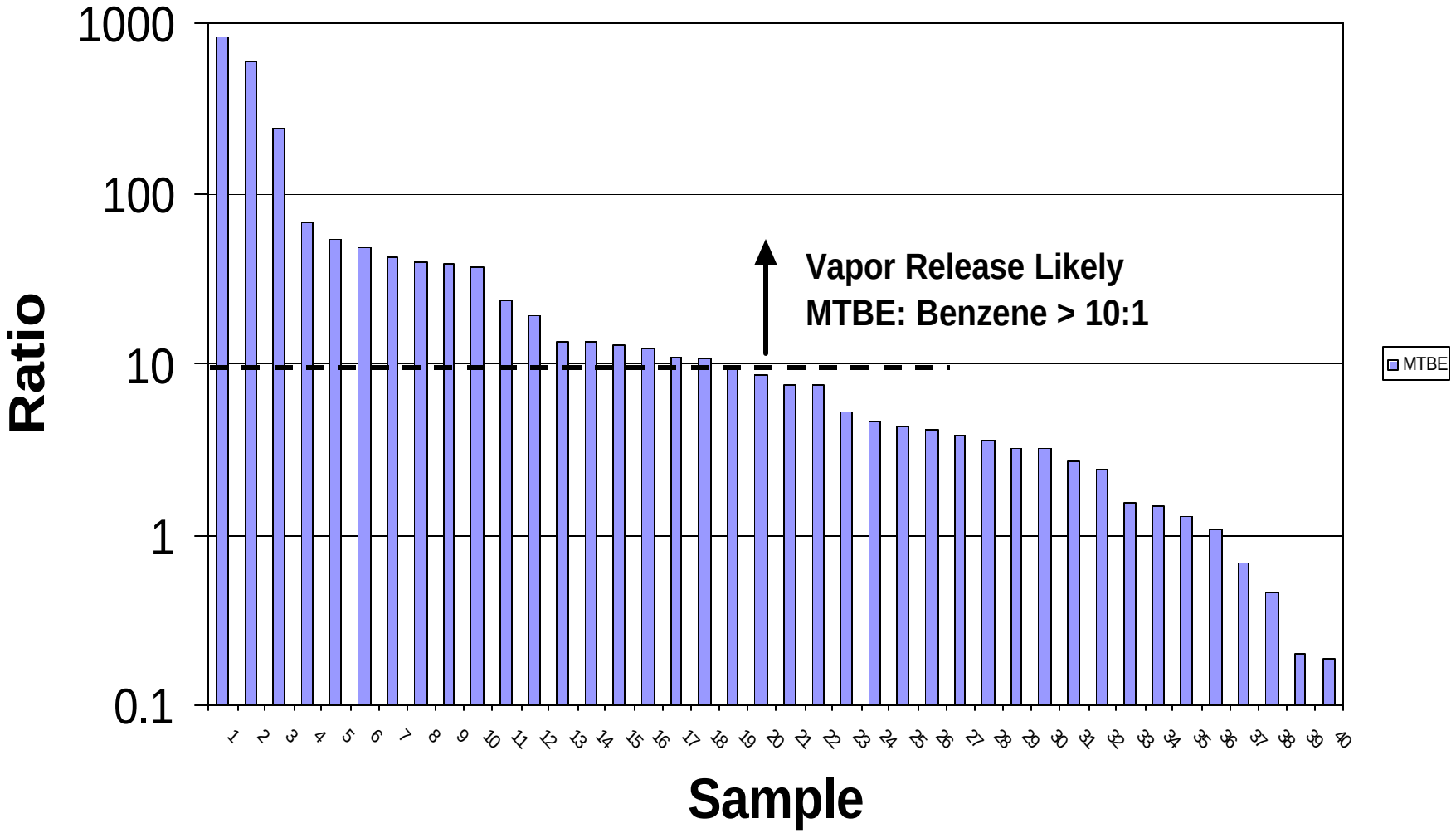
courtesy of Jim Schuck, DEH

- 12 active gas stations w/ “H numbers”
- 1997 soil vapor data at time of transaction
- Soil vapor samples at dispensers, lines, and USTs
- 92 vapor samples obtained

Soil Vapor Results

- All 12 sites w/detected MTBE
- 47% of probes encountered MTBE vapor
- range: 1480 to 357,000 ppb-v
- 72% encountered Benzene vapor
- range: 26 to 33,600 ppb-v
- ….DL for Benzene was 25 ppmv
- ….DL for MTBE was 1380 ppmv

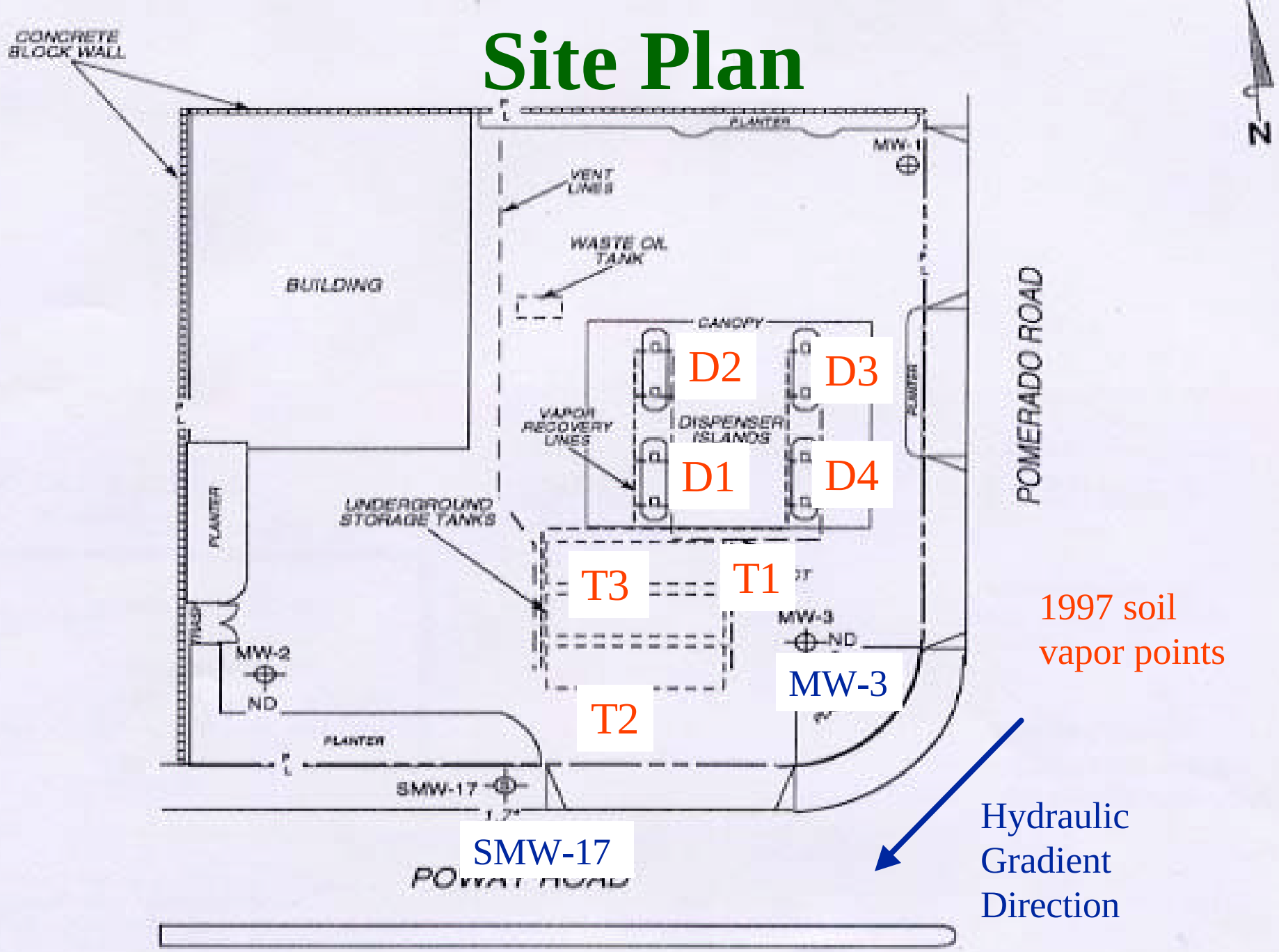
MTBE:Benzene in Vapor



Case Example: “4887”

- 9/97 Soil Vapor Survey
- Work was done in 1998 to upgrade USTs
- Groundwater at 14 to 17 ft bgs
- Gravelly sand and Silty sand overlying DG

Site Plan



1997 soil vapor points

Hydraulic Gradient Direction

Soil Vapor Data: 1997

Location	Benzene	MTBE	Ratio
	ppb-v	ppb-v	MTBE:B
T1	43	35,600	828
T2	117	ND<1380	…
T3	2290	30,300	13
D1	104	4010	39
D2	152	3570	24
D3	80	ND<1380	…
D4	90	ND<1380	…

Groundwater Data: 1999/2000

MW-3

	BTEX, ug/L	MTBE, ug/L
5/4/99	nd/nd/nd/nd	79,000
1/11/00	nd/nd/nd/nd	150,000
8/15/00	nd/nd/nd/nd	180,000

SMW-17

	BTEX, ug/L	MTBE, ug/L
5/4/99	46/2/1.7/4.6	*30,000*
1/11/00	nd/nd/nd/nd	29,000

Summary

- Yes, MTBE-only groundwater plumes can occur
- Source can be either liquid or vapor: both have similar behavior in vadose zone
- Expect MTBE:Benzene vapor > 10:1
- If soils are relatively dry, MTBE vapor will persist…and diffuse from release point
- Suggests SVE remedy may be feasible

The Future: Ethanol